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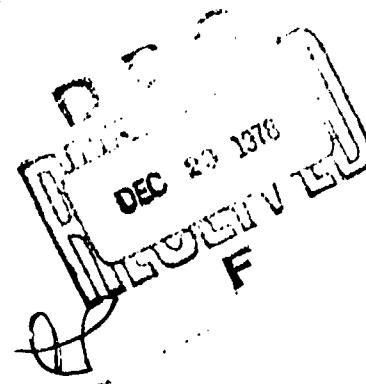
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## ANALYSIS OF OXYGEN ENRICHED AIR SAMPLES BY GAS CHROMATOGRAPHY

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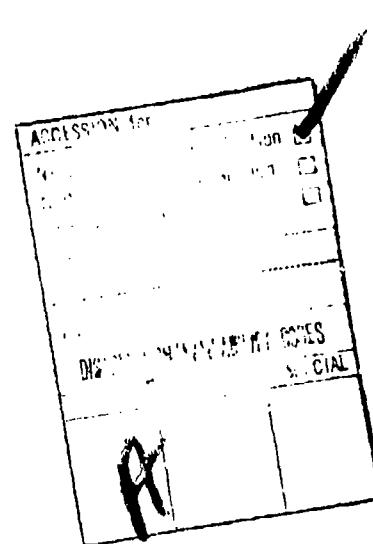
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## INTRODUCTION

This Center has been involved with the development of systems for producing breathing oxygen from ordinary air aboard an aircraft in flight, eliminating the need to store liquid oxygen. This product should ideally be close to 100% oxygen, but in reality may be somewhat less, and is termed oxygen enriched air. The Aero Materials Laboratory was requested to furnish analytical services to determine the purity of the oxygen enriched air produced by the prototype systems evaluated in Center test facilities, by the Life Support, Protection and Survival Branch of this Directorate. Several types of systems have been tested, including: molecular sieves unit, chlorate candle unit, and fluamine chelate unit.

In each case, the analytical information required included examination of the effluent gas from the test units by infrared spectroscopy to determine trace contaminants present at part per million levels (such as carbon monoxide or methane). Also required were the relative concentrations of the major components of the enriched air sample, which are normally oxygen, argon and nitrogen. In the past two years much progress has been made in this laboratory in the development of an accurate gas chromatographic method to determine percent oxygen, and when necessary, percent argon in enriched air samples.

## GENERAL DESCRIPTION OF ANALYSIS

The Hewlett-Packard model 5750 gas chromatograph was used throughout the analyses, equipped with a thermal conductivity detector and a gas sampling valve. The oven, detector and injection port temperatures were held at ambient ( $25^{\circ}\text{C}$ ). The analytical column was packed with molecular sieves 5A adsorbent. This is a synthetic zeolite material with pore diameters on the order of  $5 \times 10^{-8}$  cm (reference (a)). Molecular sieves are commonly known for their ability to separate the permanent gases, based upon molecular size exclusion and molecular configuration (reference (b)). Oxygen and nitrogen are separated readily. The Van der Walls molecular diameter of oxygen is  $2.92 \times 10^{-8}$  cm; nitrogen is  $3.15 \times 10^{-8}$  cm (reference (c)), the smaller oxygen molecules fitting into the pores of the adsorbent more readily than nitrogen, and therefore moving through the column more slowly. However, oxygen and argon ( $2.94 \times 10^{-8}$  cm) are not separable on molecular sieves, except at very long column lengths, due to their similarities in molecular size.

The sampling procedure used for the gas chromatographic analyses was to allow a pressurized sample to flow through the loop of the gas sampling valve at a flow rate of approximately 60 ml/min. Several injections were made for each sample. An equal number of standard injections were made, preferably immediately before and after the sample injections. The values obtained for separate injections were averaged to be used in the percent calculations.

## DETERMINATION OF PERCENT OXYGEN

For this analysis, helium was used as the carrier gas, with a flow rate of 40 ml/min. The optimum loop volume for the gas sampling valve was

approximately 200  $\mu$ l. This volume gave a reproducible oxygen peak on the chart paper or integrator without overloading the capacity of the column, and without the need for the use of high attenuation.

The oxygen and any argon in the sample emerge from the detector as one peak, separated from the peak due to nitrogen, if nitrogen is present (Figures 1 and 2). The initial quantitation was done using the height of the oxygen/argon peak since, under the experimental conditions used, the oxygen/argon peak emerged as a spike on the chart paper, and peak height was found to be linear with concentration. After the initial work had been completed, a graphic integrator was acquired, and now all calculations are based on integrated peak area.

For samples of enriched air generated by other than a molecular seives unit, where the concentration of oxygen relative to nitrogen was large, the contribution of argon to the oxygen/argon peak was found to be negligible.

For samples generated by the molecular seives units, however, it was assumed that the argon would be concentrated in the same proportions as the oxygen since the same factors which prevent the analytical separation of oxygen and argon would tend to concentrate them in the same proportions.

Before the method for determining argon was developed, the argon concentration could only be estimated using the relative concentrations of the two gases in normal air:  $[O_2] = 20.946\%$

$$\frac{[Ar]}{[O_2]} = \frac{0.934\%}{20.946\%}$$

$$[O_2] + [Ar] = \% \text{ determined by } O_2/\text{Ar peak} \quad (1)$$

$$[Ar] = \frac{[O_2] \cdot 0.934\%}{20.946\%} \quad (2)$$

Using the equations (1) and (2), the theoretical percentage of the argon component was calculated, and then subtracted from the value determined from the combined oxygen/argon peak, to determine percent oxygen. Now that the method for determining argon directly is available, a more accurate value is derived for percent oxygen.

The standards on which calculations were made were pure oxygen (99.99%  $O_2$ , negligible Ar and  $N_2$ ) for samples with high oxygen concentration; and room air (20.946%  $O_2$ , 0.934% Ar, and 78.084%  $N_2$ ) for low oxygen containing samples.

#### DETERMINATION OF PERCENT ARGON

The conditions for determining argon concentration are more complicated than those for determining oxygen (reference (d), Figures 3 and 4). Hydrogen is used as the carrier gas for this analysis, with a flow rate of approximately 60 ml/min. The carrier gas plus sample passes first through a stain-less steel column filled with a commercially available catalyst, 25-40 mesh size. All of the oxygen in the sample reacts with the hydrogen carrier gas to

form water in the presence of this catalyst (a precious metal alloy of the platinum group deposited on alumina). The second column is filled with molecular sieves 13X. The purpose of this column is to absorb the water generated in the first column, while allowing any argon or nitrogen present to pass through. The last column is the analytical column, filled with molecular sieves 5A, after which argon and nitrogen pass through the detector as separate peaks.

A large sample loop volume (approximately 2 ml) is needed for a direct determination of argon. Two variables were considered in the choice of the proper sample size. A sufficient volume is needed to provide enough sensitivity of detector response so that reproducible peak areas can be calculated. This is quite important for quantitation since the argon component is present at less than 5% of the total sample volume. The other factor is that a minimum sample volume is desired since a certain amount of water is generated after each sample injection. The accumulation of water eventually deactivates the catalyst and adds irreversibly to the molecular sieves columns. The smaller the sample size, the longer the columns will be useful.

The standards used for calculation of percent argon are a commercially prepared calibration mixture (4.61% Ar, 95.39% O<sub>2</sub>), room air (0.934% Ar, 20.946% O<sub>2</sub>, 78.084% N<sub>2</sub>), and pure oxygen (containing no argon). The pure oxygen is used during each analysis to verify that all oxygen is being catalytically reacted and removed from the gas stream.

#### C O N C L U S I O N S

The initial quick-response analyses to determine percent oxygen enabled personnel in the Life Support, Protection and Survival Branch to monitor the capabilities of their enriched air generating units during testing. Due to recent modifications of the analytical equipment and the addition of a graphic integrator, argon can also be determined quantitatively and even more reliable results for percent oxygen can be obtained.

#### R E C O M M E N D A T I O N S

It is recommended that the procedures described above be considered whenever methods are required for determining oxygen and argon in oxygen enriched air. They are low cost techniques, feasible for use with any gas chromatograph equipped with a thermal conductivity detector.

If the volume of sampling is expected to continue, it is recommended that additional modifications be made to the gas chromatograph in order to ease the switching of carrier gases between the oxygen and argon analyses. Also important in cutting down analysis time would be the installation of an additional sampling valve.

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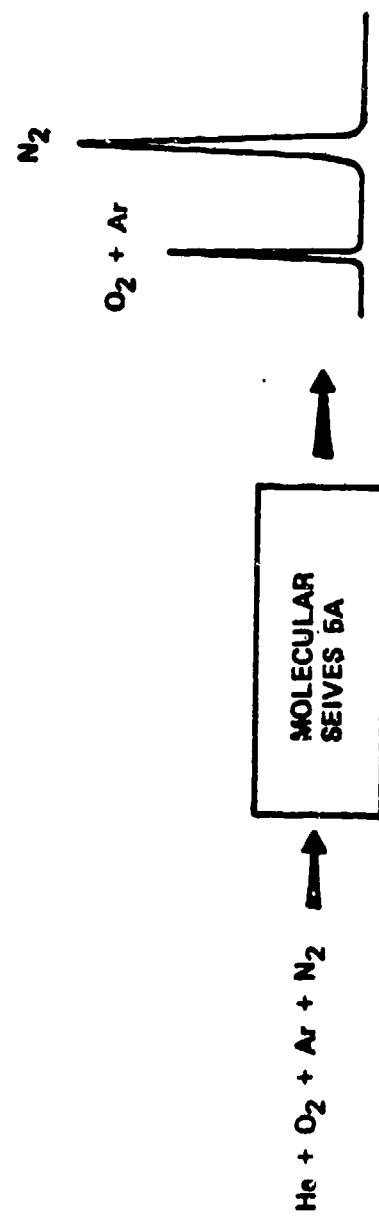


FIGURE 1. Flow Diagram of Oxygen Analysis

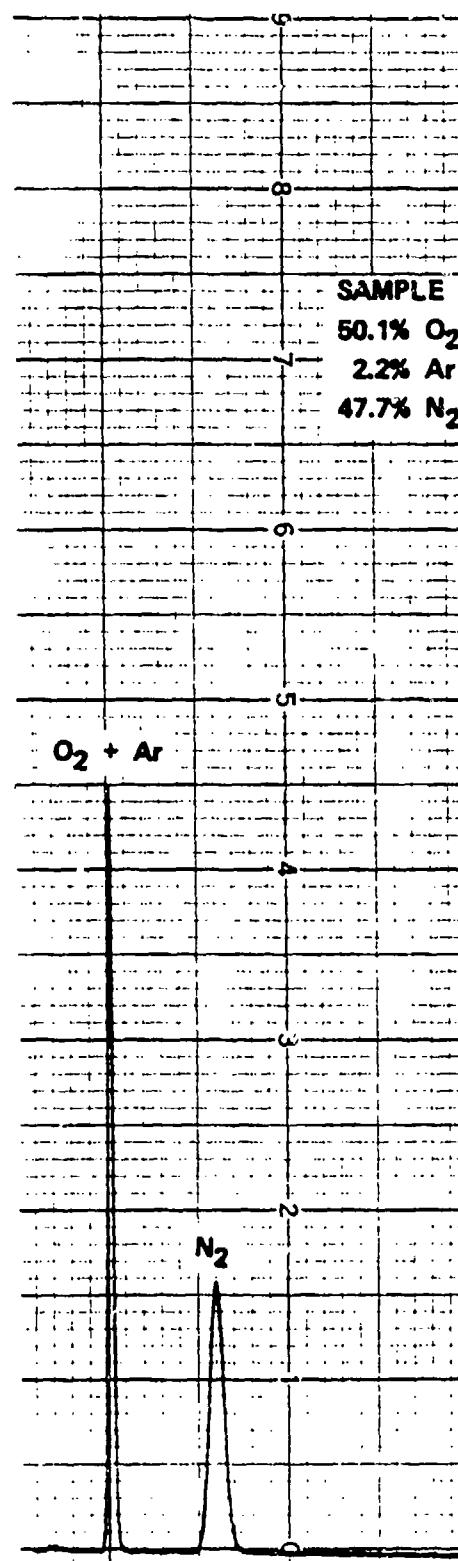
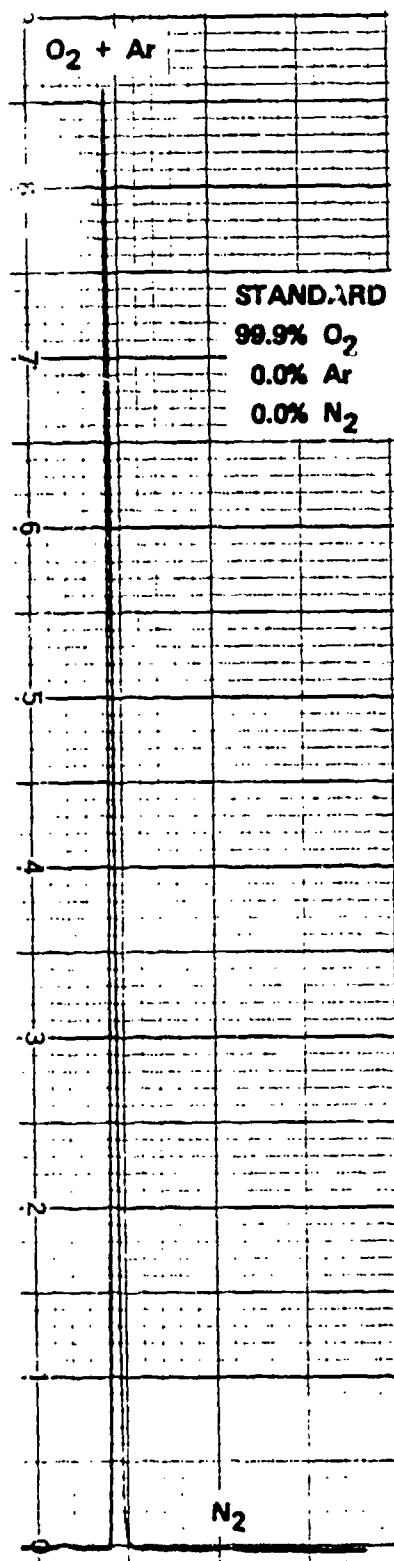


FIGURE 2. Chromatograms of Oxygen Analyses

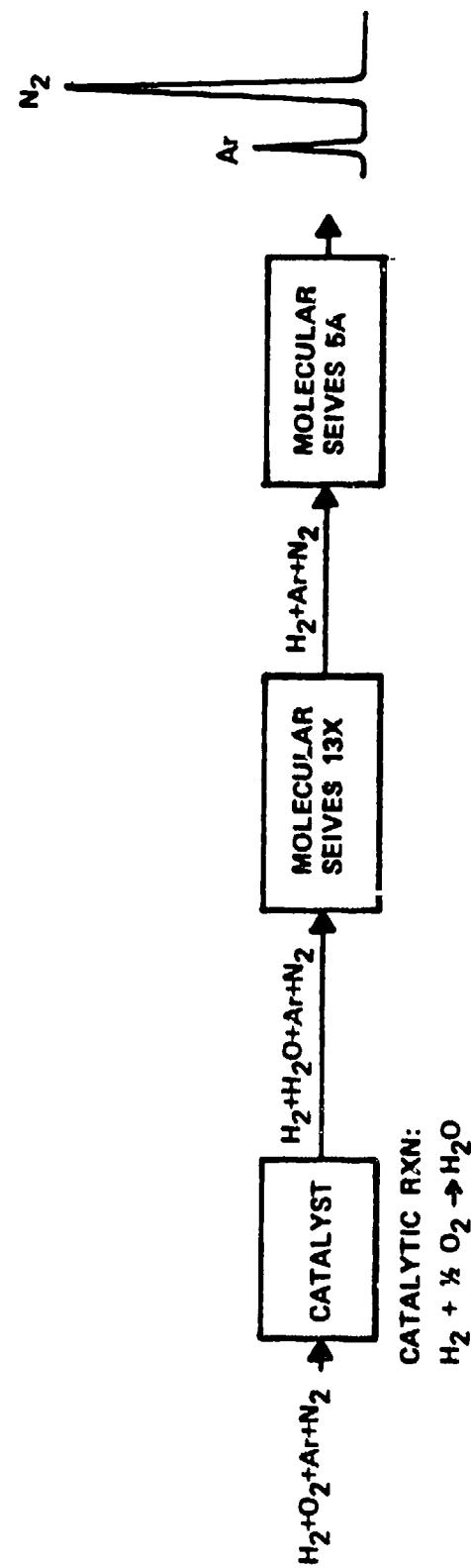


FIGURE 3. Flow Diagram of Argon Analysis



STOP

AREA %

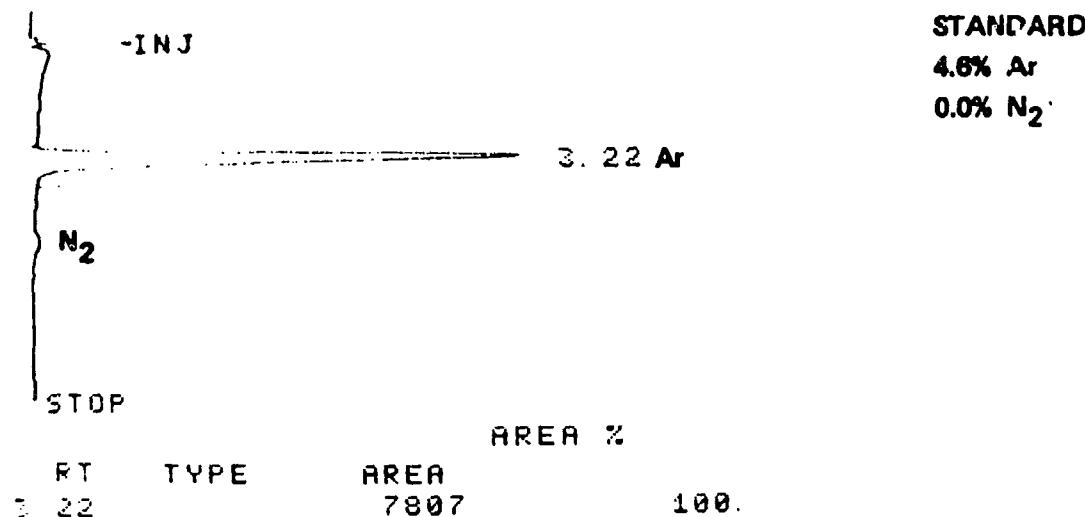
RT	TYPE	AREA	AREA %
3.22		1554	1.182
5.38		129878	98.82

HP 3380A  
DLY OFF  
MV/M .03

STOP 10

REJECT OFF

ATTN 1



HP 3380A  
DLY OFF  
MV/M .03

STOP 10

REJECT OFF

ATTN 1

FIGURE 4. Chromatograms of Argon Analyses

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